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The tribological performance of fullerene-like hydrogenated carbon films under ionic liquid lubrication

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Fullerene-like hydrogenated carbon films were deposited on Si substrate by plasma-enhanced chemical vapor deposition. The microstructures of films were characterized by high-resolution transmission electron microscopy and Raman spectrum. The tribological performance of films was tested by reciprocating ball-on-disc tester under 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid. The surface morphology and chemical composition of wear tracks and wear rates were investigated by optical microscope, X-ray photoelectron spectroscopy, and 3D surface profiler. The results indicated that the film with a typical fullerene-like structure embedded into the amorphous sp² and sp³ carbon networks could be prepared successfully, and the film shows a higher hardness (26.7 GPa) and elastic recovery (89.9%) compared with the amorphous carbon film. Furthermore, the film shows a lower friction coefficient at low contact load and friction frequency, and excellent wear-resistance performance at high load and frequency under ionic liquid lubrication. Meanwhile, the wear life of fullerene-like hydrogenated carbon films could be improved significantly using ionic liquid as a lubrication material. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: fullerene-like hydrogenated carbon film; ionic liquid; tribological performance; boundary lubrication

Introduction

Diamond-like carbon (DLC) films, as the solid lubricant materials, have been the subject of extensive research because of their excellent properties of high mechanical hardness and low friction coefficient.^[1–4] However, successful preparation and application of DLC films have been restricted by the large internal compressive stress and low elasticity.^[5] Recently, fullerene-like carbon films catch people's eye because of their unique mechanical properties, which can overcome these main drawbacks. The common characteristic of the microstructures and bond configuration in these fullerene-like carbon films is the presence of curvature in an all sp^2 3D network, constituting closed cages in the case of fullerene molecules.^[6] This unique structure makes these films hard and elastic at the same time, which results in significant improvements of the mechanical performance.^[7] From another aspect, ionic liquids (ILs), due to the strong interaction of their components through the coulomb force, have remarkable physical and chemical properties, such as inherent polarity, higher thermal stability, nonflammability, and low volatility,^[8] which make them have a greener alternative to conventional organic solvents and potential lubricants.^[9–11]

Early works in the tribological applications of ILs were mainly focused on the different types of engineering surfaces. Mu et al.[12] used ILs as the steel and aluminum friction pair and found that it was a kind of promising multifunctional lubricant. Other studies were also carried out including titanium^[13,14] and nickel alloys.^[15] These tribological studies involving ILs concern the lubrication of metallic surfaces, but ILs have strong corrosive behavior to metals.^[16] which limits the application of ILs as a lubricant material. Other materials are also of interest for scientists and engineers. Chen *et al.*^[17] investigated the tribological properties of the Boron carbon nitride (BCN) film with 1-butyl-3-methylimidazolium tetrafluoroborate IL as lubricant and found that the BCN films possessed superior tribological properties under IL lubrication, characterized by high load-carrying capacities. Sasaki^[18] combined the advantages of ILs and DLC coatings to develop a novel tribosystem for high-vacuum sliding applications and found that the friction coefficients under IL were more stable than dry sliding. González et al.[19] studied the lubrication of a Cr-DLC coating with ILs and found that ILs exhibited a friction reduction, especially at the lowest load tested. These works summarized the present understanding of the boundary lubrication of DLC coatings. So far, however, the research work on the friction of fullerene-like hydrogenated carbon (FL-C:H) films in ILs is rare. At the same time, the related work, considering the complexity of solid-liquid composite lubrication system, is very necessary.

In this work, the tribological properties of the FL-C:H films with 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) IL as lubricant is investigated systematically. The main purpose of this work is to achieve the better understanding of the solid-liquid composite lubrication system and to finally meet the requirement of the space manipulators application.

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Experimental details

Film preparation

Fullerene-like hydrogenated carbon films with thicknesses of about 1.5 μ m were prepared on Si wafer (*n*, 100) by plasmaenhanced chemical vapor deposition technology. The details about the deposition equipment were described elsewhere.^[20] A base pressure of 2.0×10^{-4} Pa was attained in the chamber with a turbo molecular pumping system. Prior to deposition, the substrates were cleaned ultrasonically in an acetone bath and dried in air and then etched by Ar plasma to remove the native oxide on the Si surface.

The specific deposition conditions of the FL-C:H films are shown in Table 1. Moreover, the amorphous carbon (*a*-C:H) films were also produced using the same deposition method (applied pulsed d.c. negative voltage 300 V, CH_4 30 sccm, and working gas pressure 27 Pa) for comparison and analysis.

1-Ethyl-3-methylimidazolium tetrafluoroborate IL (Fig. 1), as a liquid lubricant in this work, was synthesized according to the similar procedures as proposed by Hagiwara and Ito.^[21] Table 2 presents the physical properties of [Emim][BF₄] IL.

Film characterization

The high-resolution transmission electron microscopy (HRTEM) images and Raman spectra of as-deposited films were revealed by TEM (FEI Tecani F30) and Raman spectrometer (Jobin-Yvon HR-800) with an excitation wavelength of 532 nm, respectively. About 20-nm thick films were produced on single crystals of NaCl for HRTEM investigations. Plan-view samples were made by floating off the films in distilled water and placing them on Cu grids. No preparation treatments involving ion beams or chemical etch were used, which significantly reduced the possibility of introducing microstructure artifacts. The chemical states of the films were determined using a PHI-5702 multifunctional X-ray photoelectron spectroscope (XPS, operating with Al-Ka radiation and detecting chamber pressure of below 10^{-6} Pa). The mechanical properties of the films were measured by nanoindentation (Hysitron Ti-950) with a trigonal Berkowich diamond tip. The maximum indentation depth was set below 10% of the

Table 1. Summary of fullerene-like hydrogenated carbon films deposition conditions				
ltem	Parameter			
CH ₄ gas flow rate (sccm) Pulse d.c. bias (V) Deposition pressure (Pa) Duty cycle Deposition time (h)	30 1000 30 60% 3			



Figure 1. Molecular structure of the 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid.

Table 2. The physical properties of 1-ethyl-3-methylimidazolium tetra- fluoroborate ([Emim][BF ₄]) ionic liquid							
lonic liquid	Viscosity (cp) 20 °C	Density (kg/m ³)	Tg (℃)	Decomposition temperature (°C)			
[Emim][BF ₄]	45	1294	-92	412			

film thickness in order to minimize substrate influence on the film mechanical property comparison.

The friction behaviors of the films sliding against Al_2O_3 ball (5 mm in diameter) were evaluated on a reciprocating ball-on-disc tribotester with a relative humidity of about 20%. The friction tests were performed at the contact load of 2, 5, 10, 20, and 30 N under the frequency of 12 Hz. Another friction tests were performed at 6, 12, and 18 Hz at the contact load of 12 N. The wear tracks and wear rates of the films were calculated from the volume of the removed material by measuring the cross-sectional area at ten different locations along the wear track using the 3D surface profilometer. The wear rates were calculated using the equation: K = V/SL where V is the wear volume in cubic millimeters, S is the total sliding distance in meters, and L is the load in Newton.

Results and discussion

Characteristics of the as-deposited carbon film

High-resolution transmission electron microscopy is usually used to measure the nanostructure of carbon-based materials. Figure 2 displays the plan-view HRTEM micrograph of the *a*-C:H films and FL-C:H films. It is observed from Fig. 2b that the curved and cross-linked graphite arrangement is embedded in an *a*-C:H matrix. The layer spacing was about 0.34 nm, which was in good agreement with the layer spacing of the graphite face (0002).^[22] However, *a*-C:H films appeared amorphous, and no graphite arrangements were observed from Fig. 2a. These observations indicate that the film can be considered as a nanocomposite thin film with fullerene nanoparticles embedded in amorphous DLC matrix.^[23,24]

Raman spectrum is widely used to distinguish different microstructures of carbon-based films. Figure 3 presents Raman spectra of *a*-C:H film and FL-C:H film. A typical Raman spectrum of DLC films, located at the range of 800–2000 cm⁻¹, could be observed. For the *a*-C:H film, the Raman spectra of DLC films are characterized by a major peak (so-called G peak) around 1560 cm⁻¹ and a shoulder peak (D peak) around 1380 cm⁻¹.^[25] However, for the FL-C:H film, besides the D and G peaks, two extra peaks around 1200 cm⁻¹ and 1480 cm⁻¹ were also observed. Usually, the 1200 cm⁻¹ mode has a companion mode at around 1480 cm⁻¹ attributed to the fullerene or onion structure (shown in Fig. 3b).^[26-29] Namely, the films with fullerene nanostructure were deposited successfully in this work, which is in agreement with the TEM analysis.

Mechanical properties and friction behavior of as-deposited film

Nanoindentation is an attractive technique for analyzing the mechanical properties of thin films independently of the substrate. The depth of indentation was controlled to about 10% of the



Figure 2. High-resolution transmission electron microscopy plan-view image of (a) the amorphous carbon film and (b) fullerene-like hydrogenated carbon film.

film thickness. Five replicate indentations were performed. The elastic recovery was calculated by $(d_{\rm max} - d_{\rm res})/d_{\rm max} \times 100\%$, where $d_{\rm max}$ and $d_{\rm res}$ are the maximum and residual displacements, respectively. For the FL-C:H film, the elastic recovery is as high as 89.9% compared with 73.3% for the *a*-C:H film (Fig. 4). While the hardness of FL-C:H film also shows a higher value of 26.7 GPa compared with the *a*-C:H film(12.3 GPa), which may possibly be ascribed to the unique fullerene structure dispersed in *a*-C:H matrix.

Before the friction test, we also selected three different kinds of ILs: [Emim][BF₄], 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]), and 1-butyl-3-methyl imidazole double three fluorine methanesulfonyl imide salt ([Bmim][NTF₂]). The contact load is 10 N, and friction frequency is 10 Hz. It can be seen from Fig. 5 that the FL-C:H film under three kinds of ILs shows different friction coefficients: the highest friction coefficient for [Bmim][NTF₂], 0.062; then [Bmim][PF₆], about 0.051; the lowest friction coefficient



Figure 3. Raman spectra of (a) amorphous carbon film and (b) fullerenelike hydrogenated carbon film.



Figure 4. Nanoindentation load–displacement curves of the fullerene-like hydrogenated carbon (FL-C:H) film and the amorphous carbon (*a*-C:H) film.

appears in FL-C:H film under [Emim][BF₄] lubrication of 0.04. Whether lubrication in [Bmim][NTF₂] or [Bmim][PF₆], the friction coefficient curve is unstable. But for the [Emim][BF₄], the friction curve is smooth and low.



Figure 5. Friction coefficient curves of fullerene-like hydrogenated carbon film in three different ionic liquids. [Emim][BF₄], 1-ethyl-3-methylimidazolium tetrafluoroborate; [Bmim][PF₆], 1-butyl-3-methylimidazolium hexafluorophosphate; [Bmim][NTF₂], 1-butyl-3-methyl imidazole double three fluorine methanesulfonyl imide salt.

In previous study,^[30] Zhang *et al.* comparatively investigated the tribological behaviors of typical *a*-C:H film and FL-C:H film in air condition and found that the typical *a*-C:H film with the higher friction coefficient of 0.12, and the wear life were also shorter than FL-C:H film. Here, we focus on the tribological behaviors of FL-C:H film and *a*-C:H film in the lubrication of [Emim][BF₄] ILs. Figure 6 shows the *a*-C:H film and FL-C:H film under [Emim][BF₄] lubrication. The contact load is 12 N, and friction frequency is 12 Hz. It can be seen that the *a*-C:H film under [Emim][BF₄] lubrication is worn out at about 500 min (Fig. 6a). While for the FL-C:H film under [Emim][BF₄] lubrication, no worn out after sliding 10 000 min; the wear life is much longer than *a*-C:H film in [Emim][BF₄] condition (Fig. 6b), which indicates that the FL-C:H film under IL lubrication has excellent tribological behaviors than *a*-C:H film.

Based on the earlier discussion, it could be seen that the fullerene-like structure carbon film, due to its special curved structure, has shown the excellent mechanical and tribological properties; so, FL-C:H films under [Emim][BF₄] IL lubrication were investigated systematically in this study.

Figure 7 shows friction coefficient curves and average friction coefficient of the FL-C:H film at different contact loads (2, 5, 10, 20, and 30 N) in air and [Emim][BF₄] lubrication, and Fig. 8 shows friction coefficient curves and average friction coefficient of the FL-C:H film at different friction frequencies (6, 12, and 18 Hz) in air and [Emim] [BF₄] lubrication. It can be seen that the friction coefficient decreased with increasing contact load. In air, when sliding at 2 N, the FL-C:H film provides an unstable and high friction coefficient of more than 0.1, while with the increase of contact load from 2 N to 30 N, the lowest and very stable friction coefficient of about 0.02 is obtained. For the different friction frequencies, the friction coefficient shows the same trend. At 6 Hz, the highest friction coefficient of more than 0.04 could be observed, while with the friction frequency increased to 18 Hz, the lowest friction coefficient of about 0.026 is obtained. Here, the resolution of friction measurement is 0.001. This non-Amontonian friction behavior has been previously reported for DLC films^[31-33] and is also well known for other solid lubricant coatings such as MoS₂^[34] and WS₂.^[35]

However, the friction coefficient under IL lubrication shows a peculiar trend. When the FL-C:H under IL lubrication at low contact load (2 and 5 N) and low friction frequency (6 Hz), the friction coefficient is lower than the case in air condition (Figs 7c and 8c). In this condition, because of the strongly attracted atoms or molecules, the physical adsorption film may form when the solid and liquid surfaces contact. Usually, the formation of physical adsorption film occurs in the condition of normal temperature, low speed, and low load, and this may be why the film shows a lower friction coefficient at low contact load and frequency. That is to say, the film shows friction reduction ability at low contact load and frequency because of the physical adsorption. But for the high contact load (10, 20, and 30 N) and high friction frequency (12 and 18 Hz), the friction coefficient is a little bigger than the same case in air (Figs 7c and 8c). In this issue, the physical adsorption is easily desorbed, while the friction coefficient depends on the internal shear strength of the boundary film. Larger load or sliding speed will lead to the higher contact chance of the micro-convex body on the inner surface. At the same time, a large scale of adhesive contact points could be produced on the film surface, which will lead to the presence of interface adhesion. It means that larger shear force is necessary to cut off contact points and produce the relative motion, which finally cause the increase of friction coefficient.

Figure 9 shows the wear life of FL-C:H film in air condition and under IL lubrication. Figure 10 presents the wear rate of FL-C:H film in









Figure 8. Friction coefficient curves of fullerene-like hydrogenated carbon film in (a) air and (b) 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim] [BF₄]) conditions, and (c) average friction coefficient under the different sliding frequencies.

Figure 7. Friction coefficient curves of fullerene-like hydrogenated carbon (FL-C:H) film in (a) air and (b) 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) conditions, and (c) average friction coefficient under the different contact loads.

air and $[Emim][BF_4]$ conditions and the corresponding 3D profiles of wear track. The contact load is 12 N, and friction frequency is 12 Hz. It can be seen that the FL-C:H film in air condition is worn out at

about 4.5 h (Fig. 9a), at the moment the friction coefficient increases sharply, which means that the FL-C:H film is already worn out. In this case, the wear life is only 1944 m ($4.5 \times 3600 \times 0.12$). Moreover, it should be noted that the surface morphology of the wear track (Fig. 9a) corresponds to the morphology when the sliding time is 1 h. Clearly, the depth of wear track is deeper, and the wear rate is also high (about $3.78 \times 10^{-8} \text{ mm}^3/\text{Nm}$). While in IL, no worn out could be



Figure 9. The wear life of fullerene-like hydrogenated carbon film in air and 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) conditions and the corresponding profile of wear track.



Figure 10. The wear rate of fullerene-like hydrogenated carbon film in air and 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) conditions and the corresponding 3D profiles of wear track.

observed (Fig. 9b), the wear life (about 166.7 h, $\sim 7.2 \times 10^4 \text{ m}$) has already increased 37 times than in air condition. Meanwhile, the wear track is very shallow (Fig. 9b), and the wear rate is also

quite low about 4.82×10^{-10} mm³/Nm, which indicates that the FL-C:H film under IL lubrication has excellent wear resistant ability at high contact load and frequency.

XPS analysis of wear track

In order to explain why the FL-C:H film has a much longer wear life under IL lubrication, we investigated the wear track by XPS analyses to obtain further information of the chemical interactions. Prior to the XPS test, the film with wear track under IL lubrication was cleaned ultrasonically in acetone and alcohol in order to remove the residual ILs on the surface of the film. Figure 11a' displays the XPS spectrum of C1s on the original surface of the FL-C:H film. It can be fitted into three components around 284.8 and 286.2 eV. The peak around 284.8 eV corresponds to C-C bond, and the second peak around 286.2 eV corresponds to C-O bond.^[36] The XPS C1s spectrum of wear tracks in [Emim][BF₄] is exemplified in Fig. 11a. Obvious changes in the C1s spectra could be observed under [Emim][BF₄] lubrication after the tribotest is compared with the original film. The intensity of the C-C peak decreased, while the intensity of the C-O peak increased and appeared in the third peak near 288.0 eV assigned to C=O bond,^[37,38] indicating that friction oxidation reaction occurred during the sliding. It is possible lead to the destruction of the fullerene-like structure and at the same time result in the formation of oxidized polymeric layer containing carboxylic function. The oxidized polymeric layer easily yielded to sliding shear and a great deal of lubricating particle.^[39] Namely, oxygen plays an essential role in the tribological mechanism during the sliding in [Emim][BF₄].

In addition, Fig. 11b-d shows the corresponding N1s, F1s, and B1s of the wear track in [Emim][BF₄], and Fig. 11e and f shows the Al2p and O1s of the wear scar on Al_2O_3 ball. The band located at 402.4 eV assigned to N1s, which is different from pure IL [Emim][BF₄] N1s (401.5 eV) assigned to CxNy or nitrogen oxides.^[40] F1s, located at 685.9 eV, could not detect the pure IL F1s (686.6 eV), so it may belong to F^{-} ^[41] Besides, the combination of O1s (532.4 eV) and B1s (194.5 eV) speculated that it might belong to $B_2O_{3_1}^{[42]}$ which is also different from the pure IL [Emim][BF₄] B1s(193.6 eV). However, the peak of Al2p is very messy and has not found obvious Al2p signal peak (Fig. 11e). Moreover, the content of Al element is very low, only 0.28% detected, which can be ignored. Prior to the XPS test, the Al₂O₃ ball was cleaned ultrasonically in acetone and alcohol in order to remove the residual ILs on the surface of the film. So we suspect that chemical adsorption film formed on the surface of Al₂O₃ ball, which hindered the detection of Al element. That is to say the Al element does not play an important role in the case. Namely, the excellent wear-resistance performance in the friction process due to the chemical adsorption boundary lubrication film.

Taking the aforementioned into account, it was deduced that complex tribochemistry reaction proceeds on the sliding surface, resulting in the formation of CxNy, nitrogen oxides, fluoride, and boron oxide, which could be considered as the boundary lubrication film. The formed boundary lubrication film, due to chemical adsorption and molecular interactions, prevents direct contact of friction pair and, finally, causes the excellent wearresistance performance at a higher contact load or sliding frequency. The possible boundary films composition is shown in Table 3.



Figure 11. The XPS C1s peak of (a') fullerene-like hydrogenated carbon film and (a) wear track and the (b) N1s, (c) F1s, and (d) B1s of the wear track in 1-ethyl-3-methylimidazolium tetrafluoroborate, (e) Al2p, and (f) O1s of the wear scar on Al_2O_3 ball.

Table 3. The possible boundary films composition lubrication by ionic liquid							
Binding energy (eV)	N (1 s) 402.4	F (1 s) 685.9	B (1 s) 194.5	O (1 s) 532.4			
Assignation	CxNy or NxOy	F^{-}	B ₂ O ₃				

Conclusions

In the present work, FL-C:H films were successfully deposited on Si substrate by plasma-enhanced chemical vapor deposition technology. The microstructures of films were characterized by HRTEM and Raman spectrum. The tribological performances of films were tested by reciprocating ball-on-disc tester under [Emim][BF₄] IL. The surface morphology and bonding structure of wear tracks and wear rates were investigated by optical microscope, XPS, and 3D surface profiler. Several conclusions show as follows:

- (1) The fabricated films have typical fullerene-like structure, which can be seen by HRTEM and Raman spectrum.
- (2) The tribological tests demonstrated that the FL-C:H film under IL lubrication has a lower friction coefficient under at low contact load and frequency.
- (3) The FL-C:H film under IL lubrication also has an excellent wear-resistance performance at high contact and frequency (37 times than in air condition at least).
- (4) The friction mechanisms of the FL-C:H film under IL lubrication are supposed to be the formation of boundary lubrication film due to the physical and chemical adsorption during the friction.

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